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Origin of d^0 magnetism in II-VI and III-V semiconductors by substitutional doping at anion site

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By first-principles electronic structure calculations on carbon and nitrogen doped II-VI and III-V semiconductors, we demonstrate that substitutional doping at anion site by 2*p* light elements results in spontaneous spin polarization. However, to have a stable magnetic ground state, the 2*p* orbitals of the dopant must be sufficiently localized in the energy gap of the host semiconductors. The spin magnetic moment is sensitive to the relative strength of electronegativities of the dopant and the anion in the host semiconductor. Dopants with weaker electronegativity than anion in the host semiconductor should be used to produce magnetic semiconductor by anion substitutional doping with 2*p* light elements.

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Due to their promising applications in spintronics, numerous efforts have been made in recent years to synthesize dilute magnetic semiconductors (DMS) by introducing transition metal impurities in conventional semiconductors such as TiO_2 and ZnO.[1–4] Recently, unexpected room-temperature ferromagnetism was also found in two classes of semiconductors in the absence of magnetic ion dopants, which is referred as d^0 magnetism since the magnetism is not induced by the partially filled *d* orbitals.[5] One class is undoped oxides and nitrides such as CaO,[6] HfO_2,[7,8] TiO_2,[9–11] ZnO,[12] SnO_2,[13] BN and GaN,[14,15] and the other is oxides doped with 2*p* light elements, such as C- or N-doped ZnO,[16–19] SrO,[20] MgO,[21,22] and TiO_2.[23–25] These two types of ferromagnetic materials challenge our understanding of the origin of the d^0 ferromagnetism. For the first class of materials, i.e., undoped oxides and nitrides, theoretical calculations indicated that cation vacancies may be responsible for the ferromagnetism. Elfimov *et al.* first suggested that Ca vacancies in CaO can lead to a half-metallic ferromagnetic ground state.[6] Motivated by the experimental observation of the high-temperature ferromagnetism in HfO_2,[7] first-principles electronic structure calculations on HfO_2 and TiO_2 also showed that isolated cation vacancies cause formation of high-spin defect states which result in ferromagnetic ground state.[8,10,11] As in the case of oxides, cation-vacancy induced intrinsic ferromagnetism mediated by the defect states was also reported in GaN and BN.[14,15] On the other hand, the origin of ferromagnetism observed in C- or N-doped oxides has also been studied. Elfimov *et al.* proposed that substitution of nitrogen for oxygen in some oxides can produce holes in N 2*p* orbitals with local magnetic moments, which may form a ferromagnetic order.[20] Soon after, room-temperature ferromagnetism was observed in C- and N-doped ZnO, respectively.[16,17] Electronic structure calculations showed that the N and C dopants lead to spin magnetic moment, and the *p*-*d* exchangelike *p*-*p* coupling interaction was suggested to be responsible for the ferromagnetism.[16,18]

These works are significant because they demonstrate alternative ways to produce DMS. Compared to conventional magnetic semiconductors, one obvious advantage of d^0 ferromagnetism is that clusters or secondary phases formed by the dopant do not contribute to magnetism. However, despite of the studies mentioned above, the mechanism of d^0 ferromagnetism is not well understood. A complete understanding of the physics of d^0 ferromagnetism is essential for identifying robust DMS for practical applications.

In the present work, we focus on carbon or nitrogen doping in some II-VI and III-V semiconductors. First-principles electronic structure calculations based on density functional theory (DFT) were carried out to investigate the structural, electronic and magnetic properties of the doped semiconductors to probe the mechanism of ferromagnetism. We found that the magnetic properties of the semiconductors doped with 2*p* light element are determined by the fundamental physical properties such as electronegativities of the dopant and anion in the host materials. To have a stable magnetic ground state, the electronegativity of the dopant must be smaller than that of the host anion so that the 2*p* orbitals of the dopant remain localized and atomiclike. A strong interaction between the dopant and the cation of the host results in delocalization of the 2*p* states of the dopant and a nonmagnetic ground state. As the trends in different semiconductors are similar, we focus our discussion on C-doped Zn-based semiconductors in the following, and then give a summary of the results obtained in all systems we have studied.

We simulate C-doped Wurtzite-type Zn-based II-VI semiconductors Zn*X* (X=O, S, Se, and Te) using a $3\times3\times2$ supercell containing 72 atoms, which corresponds to a doping concentration of 2.78 at. % and is comparable to the experimental concentration.[16,19] The projector augmented wave (PAW) potentials were used for electron-ion interactions and generalized gradient approximation (GGA) parameterized by Perdew and Wang (PW91) was used for exchange-correlation functional.[26] The cut-off energy was 400 eV and a $3\times3\times2$ *k*-point mesh was adopted for integration in the first Brillouin zone. The cell parameters and the atomic positions of all structures were optimized until all components of the residual forces were less than 0.025 eV/Å. The accurate density of states (DOS) was calculated using the tetrahedron method with Blöchl corrections and the convergence tolerance for the self-consistent energy was set to 10^{-6} eV.

Similar to previous DFT calculations,[16] we found that before structural relaxation, all systems energetically favor a spin-polarized ground state when carbon substitutes an anion. The calculated partial density of states (PDOS) for the

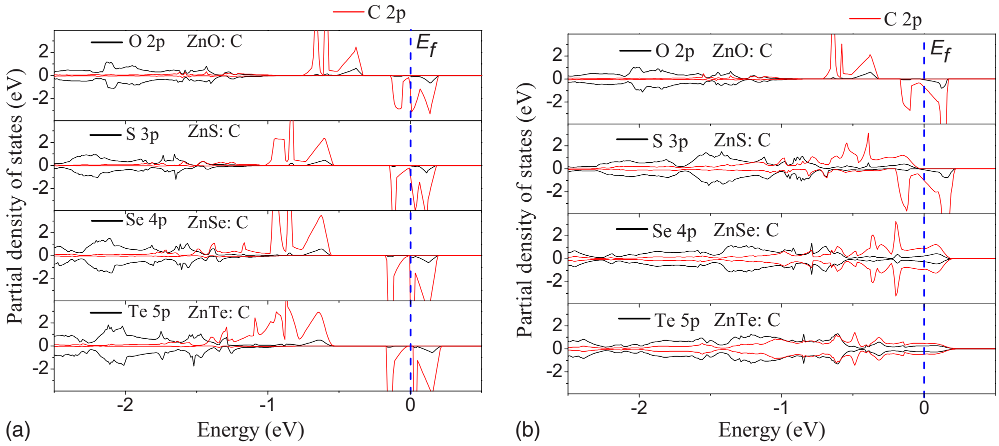

FIG. 1. (Color online) Calculated partial DOS for C-doped ZnO, ZnS, ZnSe, and ZnTe, before (a) and after (b) structural relaxation. The Fermi level is indicated by the vertical dashed line.

carbon dopant and a second-nearest neighbor anion (O, S, Se, and Te) are shown in Fig. 1(a). The atomiclike C 2*p* states are relatively localized compared to O 2*p*, S 3*p*, Se 4*p*, and Te 5*p* states. The spin-up C 2*p* states are fully occupied, while the spin-down C 2*p* states are partially filled, resulting in a total spin magnetic moment of 2.0 μ_B per carbon dopant. It is also noted that the Fermi level crosses the spin-down C 2*p* states, resulting in a half-metallic property in these Zn-based II-VI semiconductors.

After structural relaxation, the carbon 2*p* states in ZnO:C and ZnS:C remain localized at the Fermi level and ZnO:C and ZnS:C are spin-polarized, with the same magnetic moment (2.0 μ_B/atom), even though their spin-exchange splitting energy decreased. However, the magnetic moments of ZnSe:C and ZnTe:C disappeared completely. The corresponding PDOS are shown in Fig. 1(b). It is obvious that the carbon 2*p* states in ZnSe:C and ZnTe:C become delocalized and spread over the entire valence band, and the Fermi level lies just below the valence band maximum. This leads to an obvious decrease in hole states localized on carbon and the vanishing of spin magnetic moment. Therefore, by comparing the magnetic properties of C-doped ZnX, it is clear that localization of the carbon 2*p* orbital plays an important role. In ZnO:C and ZnS:C, the C 2*p* orbitals are relatively localized and the magnetic moment survives after structural optimization, while in ZnSe:C and ZnTe:C, the strong hybridization between the C 2*p* and Zn 3*d* orbitals results in delocalization of the C 2*p* orbitals and vanishing of the spin magnetic moment.

Meanwhile, relaxations of atoms around the carbon dopant were also found to be different in different semiconductors. The C–Zn bond lengths and total spin magnetic moments of the C-doped Zn*X* semiconductors before and after structural relaxations, respectively, are listed in Table I. There are two nonequivalent C–Zn bonds in Wurtzite-type Zn*X*, one along the (0001) direction and three equivalent bonds formed by C with the three nearest neighbor Zn atoms in the (0001) basal plane, as shown in the inset of Fig. 2. For convenience, we indicate the lengths of these C–Zn bonds by $d^{(1)}_{\text{C-Zn}}$ and $d^{(3)}_{\text{C-Zn}}$, respectively. Upon structural relaxation, $d^{(1)}_{\text{C-Zn}}$ increases with respect to the original O–Zn bond in the undoped ZnO, while $d^{(3)}_{\text{C-Zn}}$ experiences negligible changes. This is in agreement with experimentally observed lattice expansion.[19] For the other Zn*X* (X=S, Se and Te) doped with C, their C–Zn bond lengths decrease compared to the original Zn–*X* bond (X=S, Se, and Te), resulting in a shrink of the corresponding lattice.

To investigate the relationship between the spin polarization and the local structure around the carbon dopant, we focus on the CZn$_4$ tetrahedron in C-doped ZnS and performed a series of single-point energy calculations at different C–Zn bond lengths. In the single-point energy calculations, the T_d symmetry of the CZn$_4$ local structure and the ratio of the axial to basal C–Zn bonds were kept the same. The dependence of the calculated spin magnetic moment of C-doped ZnS on C–Zn bond length ($d^{(3)}_{\text{C-Zn}}$) is shown in Fig. 2. When the C–Zn bond is longer than about 2.12 Å, the carbon dopant induces a total spin magnetic moment of

TABLE I. C–Zn bond lengths (both in Å) and the total spin magnetic moment M (in μ_B) of C-doped Zn*X* (X=O, S, Se, and Te).

	Before Relaxation			After Relaxation		
System	$d^{(3)}_{\text{C-Zn}}$	$d^{(1)}_{\text{C-Zn}}$	M	$d^{(3)}_{\text{C-Zn}}$	$d^{(1)}_{\text{C-Zn}}$	M
ZnO	1.979	1.986	2.0	1.972	2.027	2.0
ZnS	2.356	2.361	2.0	2.116	2.040	2.0
ZnSe	2.479	2.485	2.0	2.016	1.989	0.0
ZnTe	2.670	2.679	2.0	2.001	1.991	0.0

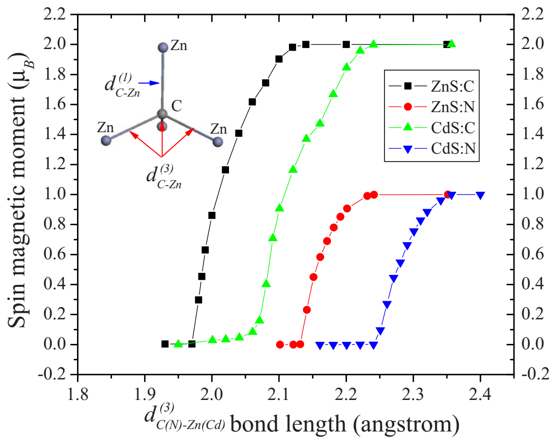

FIG. 2. (Color online) The spin magnetic moment of C-doped ZnS as a function of the C–Zn bond length. The T_d symmetry of the CZn_4 tetrahedron local structure and the ratio of axial C–Zn bond to the basal C–Zn bonds were kept the same throughout the calculation. Also shown are similar quantities of C-doped CdS, N-doped ZnO and CdS.

2.0 μ_B. But with the decrease in the C–Zn bond length, the spin magnetic moment of the system is reduced, and the magnetic moment completely vanishes when the C–Zn bond is shorter than about 1.97 Å. This indicates that formation of spin-polarized states is sensitive to the C–Zn bond length. Analysis of calculated PDOS (not shown here) of carbon dopant shows that when the C–Zn bond is long, the atomic-like C 2*p* orbital is strongly localized, and thus two holes introduced by the carbon dopant lead to a spin magnetic moment of 2.0 μ_B. When the C–Zn bond length decreases, the C–Zn bond becomes stronger due to stronger C 2*p* and Zn 3*d* hybridization, resulting in the delocalization of C 2*p* orbital. As a consequence, the change of C 2*p* orbital from localization to delocalization leads to the decrease in spin magnetic moment in C-doped ZnS. This also explains why the spin magnetic moments in C-doped ZnSe and ZnTe disappear after structural relaxation.

The C–Zn bond length is mainly determined by two factors: the size of the dopant and the relative electronegativity of the dopant and the anion atom it substitutes. In ZnO:C, the atomic radius of carbon (0.7 Å) is slightly larger than that of oxygen (0.6 Å), and the electronegativity of carbon (2.55) is much smaller than that of oxygen (3.44). These lead to the outward relaxation of Zn and a longer C–Zn bond compared to Zn–O bond in ZnO. On the other hand, in ZnTe:C, the size of the anion (1.35 Å) is much larger but its electronegativity (2.1) is much smaller than that of carbon. Therefore, the C–Zn bond shrinks from that in the unrelaxed structure (Zn–Te bond length in undoped ZnTe) during structural optimization. C–Zn bonds in both ZnS:C and ZnSe:C also become shorter after structural relaxation because of the smaller size of carbon compared to the anion atoms, even though their electronegativities are quite close. It is interesting to note that S has a slightly larger electronegativity (2.58) than carbon and the spin magnetic moment in ZnS:C survives during structural relaxation. On the other hand, the electronegativities of Se (2.55) and C are the same and the spin magnetic moment in ZnSe:C vanishes in the relaxed structure. It is also interesting to note that the degree of relaxation of the C–Zn bonds increases from O to Te, but the relaxed C–Zn bonds in different semiconductors have more or less similar lengths. This means that between atomic size and electronegativity, the latter is more important in determining the magnetic property of the ground state of a doped semiconductor. In ZnSe:C and ZnTe:C, due to the stronger C–Zn bond, more charges are transferred to the C dopant from adjacent Zn ions and anions, resulting in stronger hybridization between C 2*p* and Zn 3*d* orbitals and delocalization of C 2*p* orbital. The holes generated by the substitutional doping were originally localized mainly on the dopant. During structural relaxation, due to charge transfer to the dopant from the surrounding atoms, the empty 2*p* orbitals of the dopant are occupied by the extra charge and the holes hop to the nearby anion atoms, as can be seen from the PDOS in Fig. 1 and the calculated charge distributions.[27] Holes bounded to the anion sites are nonspin-polarized. This change of C 2*p* orbital from localization to delocalization may very well be the reason for the vanishing spin magnetic moment in C-doped ZnSe and ZnTe.

As already mentioned in previous literature,[16] the substitution of carbon for oxygen in ZnO forms a stable ferromagnetic coupling when the two substitutional C atoms were placed at the largest possible separation of 7.76 Å in a $3\times3\times2$ supercell. Further calculations[27] for various possible configurations between the two carbon dopants in the $3\times3\times2$ supercell showed that the ferromagnetic coupling between the local moments of the carbon dopants in ZnO:C is robust. Most of these configurations energetically favor parallel alignment of the local spin moments, with a total magnetic moment of 4.0 μ_B, and the energy difference between the parallel and antiparallel alignments is significant. For ZnS:C, however, the energies of the various configurations considered are very close, and the energy difference between the ferromagnetic and antiferromagnetic states is small, due mainly to the relatively delocalized sulfur 3*p* states which lead to a weak *p*-*p* coupling interaction between carbon 2*p* and sulfur 3*p* orbitals and a weak magnetic coupling in ZnS. The total magnetic moment depends sensitively on the structural configuration, and in general is reduced compared to the sum of the spin magnetic moments of two separate carbon dopants, due to the fact that in the presence of two carbon atoms within the interaction range, the C–Zn bonds are further reduced with respect to that of an isolated carbon dopant, and the stronger C–Zn bond results in the reduction in the spin magnetic moment. As a result, high carbon-doping concentration in ZnS can be expected to reduce the spin magnetic moment. Therefore, compared to ZnO:C, carbon-doping-induced spin magnetic moment may not sustain in ZnS because the C–Zn bond in ZnS:C is close to the critical value required for a stable magnetic ground state. We also estimated the Curie temperatures of ZnO:C and ZnS:C based on the mean-field theory and Heisenberg model, i.e., $k_BT_C=2E_{\mathrm{mag}}/3$.[28,29] Here E_{mag} is the magnetic energy (energy difference between FM and AFM coupling) obtained from our first-principles calculations.[27] The magnetic energy depends on separation between the dopants. Taking the highest value of E_{mag} at a doping concentration of 5.56 at. %, the highest possible T_C in ZnO:C is 454 K which is consistent

TABLE II. Difference between electronegativities of the dopant and the anion of the host semiconductor ($\Delta\chi$), and calculated spin magnetic moment per dopant (M) for Zn- and Cd-based II-VI and Ga-, Al-, and In-based III-V semiconductors doped with carbon or nitrogen.

Dopant	Anion	$\Delta\chi$	Host (μ in μ_B/atom)					
C	O	−0.89	ZnO	(2.0),	CdO	(2.0)		
	S	−0.03	ZnS	(2.0),	CdS	(2.0)		
	Se	0.00	ZnSe	(0.0),	CdSe	(2.0)		
	Te	0.45	ZnTe	(0.0),	CdTe	(1.6)		
N	O	−0.40	ZnO	(1.0),	CdO	(1.0)		
	S	0.46	ZnS	(0.0),	CdS	(0.6)		
	Se	0.49	ZnSe	(0.0),	CdSe	(0.0)		
	Te	0.94	ZnTe	(0.0),	CdTe	(0.0)		
C	N	−0.49	GaN	(1.0),	AlN	(1.0),	InN	(1.0)
	P	0.36	GaP	(0.0),	AlP	(0.0),	InP	(0.0)
	As	0.37	GaAs	(0.0),	AlAs	(0.0),	InAs	(0.0)
	Sb	0.50	GaSb	(0.0),	AlSb	(0.0),	InSb	(0.0)

with the experimental observation that the Curie temperature is above 400 K.[16] For ZnS:C, however, the estimated T_C based on the only ferromagnetic configuration is about 242 K. Therefore, we conclude that even if ZnS:C can be ferromagnetic, its Curie temperature will be below room temperature.

We also performed similar studies on carbon-doped Cd-based II-VI semiconductors, nitrogen doped Zn- and Cd-based II-VI semiconductors as well as carbon doped Ga-, Al-, and In-based III-V semiconductors, and found that the same trend between spin magnetic moment and relative electronegativity between the dopant and the anion atom is followed by all systems except the Cd-based semiconductors. As shown by the results listed in Table II, except for Cd-based II-VI systems, the doped semiconductor is magnetic if the electronegativity of the dopant is smaller than that of the anion atom of the host semiconductor. Otherwise, the system prefers a nonspin-polarized ground state. As shown in Fig. 2, the magnetic state to nonmagnetic state transition in Cd-based systems occurs at a larger C–Cd and N–Cd bond length than the corresponding C–Zn and N–Zn bond, due possibly to the large covalent radius of Cd compared to Zn. Interestingly, though In and Cd have similar covalent radii, compared with the Cd-based II-VI semiconductors, In-based III-V semiconductors follow the above trend based on electronegativity. This could be due to the fact that III-V semiconductors are more covalent while the II-VI semiconductors are more ionic. The magnetic state of a covalent semiconductor is entirely determined by the electronegativity difference between the dopant and the anion of the host, but atomic size of ionic semiconductors plays a role in its magnetic state, in addition to the electronegativity difference. Therefore, the conclusion obtained above based on carbon-doped Zn-based II-VI semiconductor may also well hold for covalent metal-compound semiconductors doped with $2p$ light elements. That is, the magnetic state of these semiconductors is determined by the relative strength of electronegativities of the dopant and the anion atom of the host material. A dopant with weaker electronegativity should always be chosen to produce magnetic semiconductor if the approach of anion substitutional doping with $2p$ light elements is taken. For less covalent systems such as Cd-based semiconductor, the relaxed bond length of dopant and cation is large enough to produce a spin moment due to the big atomic size of host atom, and the magnetic state is thus more persistent. It is noted that all known magnetic semiconductors substitutionally doped with $2p$ light elements at anion sites,[16–19,30,31] including Be-, Mg-, Ca-, Sr-, and Ti-based oxides,[20–25,32–35] comply well with this general trend.

We wish to point out that we focused mainly on the localized magnetic moment induced by substitutional doping at anion site. Issues such as magnetic exchange mechanism are not extensively discussed and doping solubility is beyond the scope of this work. However, it is worth pointing out that approaches for overcoming doping bottleneck in semiconductors have been proposed,[36] so are methods for enhancing ferromagnetic exchange coupling between the localized magnetic moments in anionogenic DMSs, and ferromagnetic stability.

In conclusion, our first-principles studies on magnetic state of Zn-based II-VI semiconductors substitutionally doped with $2p$ light elements at anion site showed that the relative strength of electronegativities of the dopant and the anion of the host semiconductor plays an important role. If the electronegativity of the dopant is much smaller than that of anion in the host (such as ZnO:C), the bond formed between the dopant with the nearest neighbor cation is relatively weak compared to the native bond between cation and anion in the host semiconductor which leads to localized atomiclike $2p$ orbital of the dopant and stable magnetic ground state. On the other hand, when the strength of the bond between the dopant and the cations of the host material increases due to larger electronegativity of the dopant compared to the anion of the host semiconductor, the $2p$ states of the dopant become delocalized and strongly hybridize with d states of the cations in the host materials, leading to a decrease and eventually vanishing of the spin magnetic moment. For carbon doping in Zn-based II-VI semiconductors, ZnO:C should be a robust magnetic semiconductor, but ZnTe:C and ZnSe:C are nonmagnetic, while ZnS:C is a borderline case and may not be an effective DMS, even though the carbon dopant generates a local magnetic moment. The same trend is followed by carbon-doped Ga-, Al-, and In-based III-V semiconductors and N-doped Zn-based II-VI semiconductors and can be expected to hold in all covalent metal-compound semiconductors/oxides doped with $2p$ light elements. The magnetic states in these systems are entirely determined by the difference between the electronegativities of the dopant and the anion in the host. However, deviation from this trend was observed in less covalent Cd-based semiconductors where the magnetic state is more persistent.

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[1] Y. Matsumoto, M. Murakami, T. Shono, T. Hasegawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S.-y. Koshihara, and H. Koinuma, Science **291**, 854 (2001).

[2] K. A. Griffin, A. B. Pakhomov, C. M. Wang, S. M. Heald, and K. M. Krishnan, Phys. Rev. Lett. **94**, 157204 (2005).

[3] M. Venkatesan, C. B. Fitzgerald, J. G. Lunney, and J. M. D. Coey, Phys. Rev. Lett. **93**, 177206 (2004).

[4] Q. Xu, H. Schmidt, L. Hartmann, H. Hochmuth, M. Lorenz, A. Setzer, P. Esquinazi, C. Meinecke, and M. Grundmann, Appl. Phys. Lett. **91**, 092503 (2007).

[5] J. M. D. Coey, Solid State Sci. **7**, 660 (2005).

[6] I. S. Elfimov, S. Yunoki, and G. A. Sawatzky, Phys. Rev. Lett. **89**, 216403 (2002).

[7] M. Venkatesan, C. B. Fitzgerald, and J. M. D. Coey, Nature (London) **430**, 630 (2004).

[8] C. D. Pemmaraju and S. Sanvito, Phys. Rev. Lett. **94**, 217205 (2005).

[9] N. H. Hong, J. Sakai, N. Poirot, and V. Brizé, Phys. Rev. B **73**, 132404 (2006).

[10] K. Yang, Y. Dai, B. Huang, and Y. P. Feng, Phys. Rev. B **81**, 033202 (2010).

[11] H. Peng, J. Li, S.-S. Li, and J.-B. Xia, Phys. Rev. B **79**, 092411 (2009).

[12] N. H. Hong, J. Sakai, and V. Brizé, J. Phys.: Condens. Matter **19**, 036219 (2007).

[13] N. H. Hong, N. Poirot, and J. Sakai, Phys. Rev. B **77**, 033205 (2008).

[14] P. Dev, Y. Xue, and P. Zhang, Phys. Rev. Lett. **100**, 117204 (2008).

[15] H. Jin, Y. Dai, B. Huang, and M.-H. Whangbo, Appl. Phys. Lett. **94**, 162505 (2009).

[16] H. Pan, J. B. Yi, L. Shen, R. Q. Wu, J. H. Yang, J. Y. Lin, Y. P. Feng, J. Ding, L. H. Van, and J. H. Yin, Phys. Rev. Lett. **99**, 127201 (2007).

[17] C.-F. Yu, T.-J. Lin, S.-J. Sun, and H. Chou, J. Phys. D **40**, 6497 (2007).

[18] L. Shen, R. Q. Wu, H. Pan, G. W. Peng, M. Yang, Z. D. Sha, and Y. P. Feng, Phys. Rev. B **78**, 073306 (2008).

[19] S. Zhou, Q. Xu, K. Potzger, G. Talut, R. Grotzschel, J. Fassbender, M. Vinnichenko, J. Grenzer, M. Helm, H. Hochmuth, M. Lorenz, M. Grundmann, and H. Schmidt, Appl. Phys. Lett. **93**, 232507 (2008).

[20] I. S. Elfimov, A. Rusydi, S. I. Csiszar, Z. Hu, H. H. Hsieh, H.-J. Lin, C. T. Chen, R. Liang, and G. A. Sawatzky, Phys. Rev. Lett. **98**, 137202 (2007).

[21] A. Droghetti and S. Sanvito, Appl. Phys. Lett. **94**, 252505 (2009).

[22] B. Gu, N. Bulut, T. Ziman, and S. Maekawa, Phys. Rev. B **79**, 024407 (2009).

[23] K. Yang, Y. Dai, B. Huang, and M.-H. Whangbo, Appl. Phys. Lett. **93**, 132507 (2008).

[24] Y. Bai and Q. Chen, Solid State Commun. **147**, 169 (2008).

[25] K. Yang, Y. Dai, B. Huang, and M.-H. Whangbo, Chem. Phys. Lett. **481**, 99 (2009).

[26] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[27] See supplementary material at http://link.aps.org/supplemental/10.1103/PhysRevB.81.125211 for charge distributions, magnetic exchange coupling and estimated Curie temperature for C-doped ZnO and ZnS.

[28] J. Kudrnovský, I. Turek, V. Drchal, F. Máca, P. Weinberger, and P. Bruno, Phys. Rev. B **69**, 115208 (2004).

[29] F. Máca, J. Kudrnovský, V. Drchal, and G. Bouzerar, Appl. Phys. Lett. **92**, 212503 (2008).

[30] R. Long and N. J. English, Phys. Rev. B **80**, 115212 (2009).

[31] H. Pan, Y. P. Feng, Q. Y. Wu, Z. G. Huang, and J. Lin, Phys. Rev. B **77**, 125211 (2008).

[32] K. Kenmochi, M. Seike, K. Sato, A. Yanase, and H. Katayama-Yoshida, Jpn. J. Appl. Phys. **43**, L934 (2004).

[33] K. Kenmochi, V. A. Dinh, K. Sato, A. Yanase, and H. Katayama-Yoshida, J. Phys. Soc. Jpn. **73**, 2952 (2004).

[34] V. A. Dinh, M. Toyoda, K. Sato, and H. Katayama-Yoshida, J. Phys. Soc. Jpn. **75**, 093705 (2006).

[35] I. R. Shein, M. V. Ryzhkov, M. A. Gorbunova, Y. N. Makurin, and A. L. Ivanovskii, JETP Lett. **85**, 246 (2007).

[36] S.-H. Wei, Comput. Mater. Sci. **30**, 337 (2004).